

Thermodynamic Property Relations

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ME 407: Advanced Thermodynamics

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Overview

1 Thermodynamic Property Relations



Thermodynamic Property Relations

Mathematical Theorems

- If there exists a relation among x , y & z ; $\rightarrow f(x, y, z) = 0$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1$$

- $f(x, y, z) = 0 \rightarrow z = z(x, y)$, $y = y(z, x)$, $x = x(y, z)$

$$z = z(x, y) \rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = Mdx + Ndy$$

For continuous functions, $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \Rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$



Thermodynamic Property Relations

Maxwell's Relationships

- Internal Energy, $du = \delta q + \delta w = Tds - Pdv$ (for rev. process)
- Enthalpy, $h \equiv u + Pv \Rightarrow dh = du + Pdv + v dP = Tds + v dP$
- Helmholtz Energy, $f \equiv u - Ts \Rightarrow df = -Pdv - s dT$
- Gibbs Energy, $g \equiv h - Ts \Rightarrow dg = dh - Tds - s dT = v dP - s dT$

For continuous functions, $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \Rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

$$1 \quad du = +Tds - Pdv \Rightarrow \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \dots \dots \dots (M01)$$

$$2 \quad dh = +Tds + v dP \Rightarrow \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \dots \dots \dots (M02)$$

$$3 \quad df = -s dT - Pdv \Rightarrow \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \dots \dots \dots (M03)$$

$$4 \quad dg = -s dT + v dP \Rightarrow \left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P \dots \dots \dots (M04)$$



Heat Capacity at Constant Volume, C_v

- $du = Tds - Pdv \Rightarrow \left(\frac{\partial u}{\partial s}\right)_v = T$
- $C_v \equiv \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$
- $\left(\frac{\partial C_v}{\partial v}\right)_T = \frac{\partial}{\partial v} \left[T \left(\frac{\partial s}{\partial T}\right)_v \right] = T \frac{\partial^2 s}{\partial v \partial T} = T \frac{\partial}{\partial T} \left[\frac{\partial s}{\partial v} \right]_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_v$
using Maxwell's relation: $\left(\frac{\partial s}{\partial v}\right)_T = + \left(\frac{\partial P}{\partial T}\right)_v$

If P-v-T data or mathematical relationship is available, it is possible to evaluate $\partial^2 P / \partial T^2$, and then $(\partial C_v / \partial v)_T$.

- Ideal gas: $Pv = RT$
 $\Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$ & $\left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0 \rightarrow C_v \neq f(v)$
- van der Wall's gas: $P = \frac{RT}{v-b} - \frac{a}{v^2}$
 $\Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$ & $\left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0 \rightarrow C_v \neq f(v)$



Heat Capacity at Constant Pressure, C_p

- $dh = Tds + vdP \Rightarrow \left(\frac{\partial h}{\partial s}\right)_P = T$
- $C_p = \left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{\partial h}{\partial s}\right)_P \left(\frac{\partial s}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P$
- $\left(\frac{\partial C_p}{\partial P}\right)_T = \frac{\partial}{\partial P} \left[T \left(\frac{\partial s}{\partial T}\right)_P \right] = T \frac{\partial}{\partial T} \left[\frac{\partial s}{\partial P} \right]_T = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_P$
using Maxwell's relation: $\left(\frac{\partial s}{\partial P}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_P$
- Ideal gas: $\Rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$ & $\left(\frac{\partial^2 v}{\partial T^2}\right)_P = 0 \rightarrow C_p \neq f(P)$
- van der Wall's gas: $\Rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P - \frac{a}{v^2} \left(1 - \frac{2b}{v}\right)}$
 $\left(\frac{\partial^2 v}{\partial T^2}\right)_P = - \frac{R^2 \left(\frac{2a}{v^3} - \frac{6ab}{v^4}\right)}{\left(P - \frac{a}{v^2} \left(1 - \frac{2b}{v}\right)\right)^3} \rightarrow C_p = f(P) = \int_{P_1}^{P_2} -T \left(\frac{\partial^2 v}{\partial T^2}\right)_P dP$



Tds Relationships

- $s = s(v, T) \rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$
 $C_v = T \left(\frac{\partial s}{\partial T}\right)_v$ & $\left(\frac{\partial s}{\partial v}\right)_T = + \left(\frac{\partial P}{\partial T}\right)_v$, Maxwell's Relation (C)
 $Tds = C_v dT + T \left(\frac{\partial P}{\partial T}\right)_v dv$ (1st Tds)
- $s = s(P, T) \rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$
 $C_p = T \left(\frac{\partial s}{\partial T}\right)_P$ & $\left(\frac{\partial s}{\partial P}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_P$, Maxwell's Relation (D)
 $Tds = C_p dT - T \left(\frac{\partial v}{\partial T}\right)_P dP$ (2nd Tds)
- $s = s(P, v) \rightarrow ds = \left(\frac{\partial s}{\partial P}\right)_v dP + \left(\frac{\partial s}{\partial v}\right)_P dv$
 $C_v = T \left(\frac{\partial s}{\partial T}\right)_v$ & $C_p = T \left(\frac{\partial s}{\partial T}\right)_P$
 $Tds = C_v \left(\frac{\partial T}{\partial P}\right)_v dP + C_p \left(\frac{\partial T}{\partial v}\right)_P dv$ (3rd Tds)



Internal Energy, u

- $u = u(v, T) \rightarrow du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv = C_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$
- $du = Tds - Pdv = C_v dT + T \left(\frac{\partial P}{\partial T}\right)_v dv - Pdv$ (\leftrightarrow 1st Tds Eq.)
 $\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_v - P$
 $du = C_v dT + [T \left(\frac{\partial P}{\partial T}\right)_v - P] dv$
- Ideal gas: $\left(\frac{\partial u}{\partial v}\right)_T = \left[\frac{RT}{v} - P\right] = 0$
 $\left(\frac{\partial u}{\partial v}\right)_T = 0 = \left(\frac{\partial u}{\partial P}\right)_T \left(\frac{\partial P}{\partial v}\right)_T = -\frac{P}{v} \left(\frac{\partial u}{\partial P}\right)_T \rightarrow \left(\frac{\partial u}{\partial P}\right)_T = 0$
 $\left(\frac{\partial u}{\partial v}\right)_T = 0 \rightarrow u \neq f(v): \left(\frac{\partial u}{\partial P}\right)_T = 0 \rightarrow u \neq f(P)$
 $\rightarrow du = C_v dT = f(T)$
- van der Waals' gas:
 $\left(\frac{\partial u}{\partial v}\right)_T = \frac{RT}{v-b} - P = \frac{a}{v^2} \rightarrow du = C_v dT + \frac{a}{v^2} dv = f(T, v)$



Enthalpy, h

- $h = h(P, T) \rightarrow dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP = C_p dT + \left(\frac{\partial h}{\partial P}\right)_T dP$
- $dh = T ds + dP = C_p dT - T \left(\frac{\partial v}{\partial T}\right)_P dP + v dP$ ($\leftarrow 2^{nd} Tds$ Eqn.)

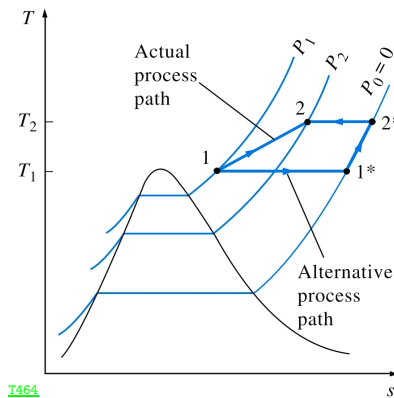
$$\left(\frac{\partial h}{\partial P}\right)_T = v - T \left(\frac{\partial v}{\partial T}\right)_P$$

$$dh = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

- Ideal gas: $\left(\frac{\partial h}{\partial P}\right)_T = v - \frac{TR}{P} = 0 \rightarrow h \neq f(P)$
 $\left(\frac{\partial h}{\partial P}\right)_T = 0 = \left(\frac{\partial h}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T = -\frac{v}{P} \left(\frac{\partial h}{\partial v}\right)_T \rightarrow \left(\frac{\partial h}{\partial v}\right)_T = 0$
 $\left(\frac{\partial h}{\partial P}\right)_T = 0 \rightarrow h \neq f(P): \quad \left(\frac{\partial h}{\partial v}\right)_T = 0 \rightarrow h \neq f(v)$

$$\rightarrow dh = C_p dT = f(T)$$

- van der Waals' gas: $\Rightarrow h = f(T, P)$



- for isobar: $\Rightarrow dh_P = C_p dT_P$
- for isotherm: $\Rightarrow dh_T = \left[v - T \left(\frac{\partial v}{\partial T}\right)_P\right] dP_T$

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$$\begin{aligned} h_2 - h_1 &= (h_2 - h_2^*) + (h_2^* - h_1^*) + (h_1^* - h_1) \\ &= \int_{P_0}^{P_2} \left[v - T \left(\frac{\partial v}{\partial T}\right)_P\right]_{T_2} dP + \int_{T_1}^{T_2} C_{P_0} dT_P \\ &\quad - \int_{P_0}^{P_1} \left[v - T \left(\frac{\partial v}{\partial T}\right)_P\right]_{T_1} dP \end{aligned}$$



Heat Capacity Equations

- $s = s(v, T) \rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$
 $\left(\frac{\partial s}{\partial T}\right)_P = \left(\frac{\partial s}{\partial T}\right)_v + \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \leftarrow \left[\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_p}{T}, \left(\frac{\partial s}{\partial v}\right)_T = \frac{C_v}{T}\right]$
 $\rightarrow C_p - C_v = T \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P = T \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P$

- $f(x, y, z) = 0 \rightarrow \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial x}{\partial y}\right)_z = -1$
 $\rightarrow \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial T}{\partial P}\right)_v \left(\frac{\partial v}{\partial T}\right)_P = 1 \rightarrow \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_v$

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P = -T \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P^2$$

- 1 For liquids & solids, $\left(\frac{\partial v}{\partial T}\right)_P \rightarrow 0 \Rightarrow C_p \approx C_v \approx C$
- 2 $\left(\frac{\partial v}{\partial T}\right)_P^2$ is +ve & $\left(\frac{\partial P}{\partial v}\right)_T$ is -ve for all known substances, $C_p \geq C_v$
- 3 as $T \rightarrow 0$, $C_p \rightarrow C_v$, at $T = 0$, $C_p = C_v$



- Isothermal compressibility, $k_T \equiv -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T$
- Volume expansivity, $\beta \equiv \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$

$$C_p - C_v = -T \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P^2 = \frac{\beta^2}{k_T} v T$$

- Ideal gas: $Pv = RT \rightarrow k_T = \frac{1}{P}$, $\beta = \frac{1}{T} \Rightarrow C_p - C_v = R$
- for liquid water at 1 bar:

T (°C)	Density (kg/m ³)	$\beta \times 10^6$ (K) ⁻¹	$\kappa \times 10^6$ (bar) ⁻¹
0	999.84	-68.14	50.89
10	999.70	87.90	47.81
20	998.21	206.6	45.90
30	995.65	303.1	44.77
40	992.22	385.4	44.24
50	988.04	457.8	44.18

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 $\beta = 0.0 @ 4^\circ\text{C}$ for water.


Example: Liquid Water 1 atm & 20°C

- $C_P - C_V = \frac{\beta^2}{k_T} v T = \frac{(206.6 \times 10^{-6} \frac{1}{K})^2}{45.95 \times 10^{-6} \frac{1}{bar}} \frac{1}{998.21 \frac{kg}{m^3}} (293K) \left| \frac{10^5 \frac{N}{m^2}}{1bar} \right|$
 $C_P - C_V = 27.29 \frac{J}{kg \cdot K}, \therefore C_P = 4188 \frac{J}{kg \cdot K} \mapsto C_P \simeq C_V$
- $P = P(v, T) \rightarrow dP = \left(\frac{\partial P}{\partial T}\right)_v dT + \left(\frac{\partial P}{\partial v}\right)_T dv = \frac{\beta}{k_T} dT - \frac{1}{k_{TV}} dv$

$$dP = \frac{\beta}{k_T} dT - \frac{1}{k_{TV}} dv$$

- If liquid water temperature is raised from 19.5 to 20.5°C at constant volume: $dP = \frac{\beta}{k_T} dT \mapsto \Delta P = \frac{\beta}{k_T} \Delta T$

$$\Delta P = \frac{206.6 \times 10^{-6} \frac{1}{K}}{45.95 \times 10^{-6} \frac{1}{bar} \cdot 10^2 \frac{kPa}{bar}} (1K) = 450 \text{ kPa}$$

Applications of Tds Relationships

$$2^{nd} Tds : \dots \quad Tds = C_P dT - T \left(\frac{\partial v}{\partial T}\right)_P dP$$

- Reversible isothermal change in pressure:

$$\rightarrow Tds = -T \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$\Rightarrow q = -T \int \left(\frac{\partial v}{\partial T}\right)_P dP = -T \int \beta v dP = -T \bar{v} \beta \Delta P$$

$$\Rightarrow w = -\int P dv = -\int \left(\frac{\partial v}{\partial P}\right)_T P dP = \int_{P_1}^{P_2} v k_T P dP = \frac{\bar{v} k_T}{2} (P_2^2 - P_1^2)$$

for a liquid & solid, v , β & k_T are insensitive to change in P

- Reversible adiabatic change in pressure:

$$\rightarrow dT = \frac{T}{C_P} \left(\frac{\partial v}{\partial T}\right)_P dP = \frac{T v \beta}{C_P} dP \Rightarrow \Delta T = \frac{T \bar{v} \beta}{C_P} \Delta P$$

Experiments show that C_P hardly changes for a solid & liquid even for an increase of 10,000 bar.

Example: 15 cm³ Hg @0°C & 1 bar → 1000 bar

at 0°C $\bar{V} = 1.5 \times 10^{-5} m^3$ $\bar{C}_P = 28.6 J/K$
 $\bar{\beta} = 178 \times 10^{-6} K^{-1}$ $\bar{k}_T = 3.88 \times 10^{-6} bar^{-1}$

- isothermal compression: $P_1 = 1 \text{ bar}, P_2 = 1000 \text{ bar}.$

$$\Rightarrow Q = mq = -T(m\bar{v})\bar{\beta}\Delta P = -T\bar{V}\bar{\beta}\Delta P = \underline{-78.2 \text{ J}}$$

$$\Rightarrow W = mw = \frac{\bar{V} k_T}{2} (P_2^2 - P_1^2) = \underline{2.91 \text{ J}}$$

$$\Rightarrow \Delta U = Q + W = \underline{-75.29 \text{ J}}$$

- 78.2 J heat is liberated but only 2.91 J work is done. The extra amount of heat comes from the store of the internal energy.
- For a substance with a negative expansivity, heat is absorbed and the internal energy is increased.

- isentropic compression: $P_1 = 1 \text{ bar}, P_2 = 1000 \text{ bar}.$

$$\Rightarrow \Delta T = \frac{T \bar{v} \bar{\beta}}{C_P} \Delta P = \underline{2.55 \text{ K}}$$



Clausius-Clapeyron Equation (for Phase Change)

- $\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T = \frac{s_2 - s_1}{v_2 - v_1}$: phase change $\rightarrow T = T_{sat} = \text{const.}$

- $\left(\frac{\partial P}{\partial T}\right)_v = \frac{dP}{dT}$, for mixture of 2 phases, $P = f(T)$

$$\bullet \frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{h_2 - h_1}{T(v_2 - v_1)} \Rightarrow \boxed{\frac{dP}{dT}}_{sat} = \frac{h_{12}}{T v_{12}} \text{ Clapeyron Eqn.}$$

Example: using only P-v-T data, estimate h_{fg} of R-134a at 20°C

$$\bullet v_{fg} = (v_g - v_f)_{sat, @20^\circ C} = 0.035153 m^3/kg$$

$$\bullet \left(\frac{dP}{dT}\right)_{sat, @20^\circ C} = \frac{\Delta P}{\Delta T} \Big|_{sat, @20^\circ C} = \frac{P_{sat, @24^\circ C} - P_{sat, @16^\circ C}}{24^\circ C - 16^\circ C} = 17.70 \text{ kPa/K}$$

$$\bullet h_{fg} = T v_{fg} \left(\frac{dP}{dT}\right)_{sat, @20^\circ C} = (293.15)(0.035153)(17.70) = 182.40 \text{ kJ/kg}$$

Tabulated value of h_{fg} @20°C is 182.27 kJ/kg.

- $v_2 \gg v_1 \rightarrow v_2 = \frac{RT}{P} \Rightarrow \boxed{\left(\frac{d \ln P}{d(1/T)}\right)_{sat}} = -\frac{h_{fg}}{R}$ Clausius-Clapeyron Eq.

$$\rightarrow \ln \left(\frac{P_2}{P_1}\right)_{sat} = \frac{\Delta h}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- $\ln P_{sat} = A + \frac{B}{T} + C \ln T + DT$, widely used vapour-pressure Eq.

